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<p>(21) International Application Number: PCT/US93/12483 (22) International Filing Date: 20 December 1993 (20.12.93) (30) Priority Data: 07/999,042 31 December 1992 (31.12.92) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: ORIANI, Steven, R.; 1002 E. Park Drive, Midland, MI 48640 (US). (74) Agent: GALBRAITH, Ann, K.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).</p>		<p>(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report. With amended claims.</p>
<p>(54) Title: THERMOPLASTIC POLYURETHANES AND A PROCESS FOR THEIR PREPARATION (57) Abstract Described herein is a thermoplastic polyurethane elastomer prepared by a reactive extrusion process from a reaction mixture comprising (a) a polyisocyanate; (b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an equivalent weight of at least about 500; and (c) diethylene glycol; wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1, and the ratio of isocyanate groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05. The composition of the invention provides an extrusion grade thermoplastic polyurethane resin produced by a one-shot process. The resin has a stable crystalline melting point and can be thermally processed and extruded into films or other profiles which are substantially free of gels.</p>		

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THERMOPLASTIC POLYURETHANES  
AND A PROCESS FOR THEIR PREPARATION

This invention relates to thermoplastic polyurethane elastomers and, more particularly, to thermoplastic polyurethane elastomers prepared from polyether polyols.

Thermoplastic polyurethane (TPU) resins are essentially linear polymers which can be thermally processed by techniques such as melt-extrusion, compression molding and injection molding. Typically, TPU resins are prepared by reacting a polyol with an organic polyisocyanate, preferably a diisocyanate, usually in the presence of a low molecular weight difunctional chain-extending agent. It is generally accepted that a TPU resin has a polymer morphology comprising "hard" and "soft" segments. Hard segments are molecular entities derived from reaction of the chain-extending agent with isocyanate. Soft-segments are derived from the polyol/isocyanate reaction.

At temperatures where TPU resins exhibit useful mechanical properties, a microphase separation exists between the hard and soft segments. Soft-segments can be considered as having glass transition temperatures below room temperature while hard-segments can be considered as having a glass transition and crystalline melting point temperature above room temperature. Structure-property relationships of hard- and soft-segment phases are described, for example, by Redman in "Developments in Polyurethanes-I" J.M. Buist Ed., Elsevier, London (1978). During melt processing, however, the TPU resin typically exists in a single phase state. From a processing standpoint, it is desirable for the TPU resin to be "stable" at processing temperatures (for example 200°C), that is, for the melting point of the hard-segment to not significantly increase, over a period of at least about 30 minutes. If the melting point does increase, crystallites, or "gels," may form in the resin during processing. TPU resins whose crystalline melting points increase by more than 10°C over such a period are difficult to process since the residence time distribution of a polymer in an extrusion process at elevated temperatures virtually assures that at least a small fraction of the resin will remain in the barrel or die long enough to crystallize. Crystallized resin then typically builds up in the extruder until chunks are broken free by the melt stream and carried through the die, where they form defects in the extrudate, clog narrow die gaps, or plug the screen pack in the extruder.

The preparation of thermoplastic polyurethane elastomers from polyester polyols is well-known in the art. Such elastomers can be extruded, injection molded, or otherwise processed at elevated temperatures without significant change in the degree of phase separation of the hard and soft domains of the polymers, which would otherwise cause portions of the polymer to crystallize during the thermal processing.

Thermoplastic polyurethanes (TPUs) prepared from 4,4'-diphenyl methane diisocyanate (MDI), a 1,4-butanediol (BDO) chain extender and poly(tetramethylene ether)

glycol, are also well-known and are described, for example, in U.S. Patent 3,642,964. These materials can be easily molded and extruded due to their rapid development of microphase separation upon quenching from the melt, and due to their resistance to degradation caused by prolonged exposure to processing temperatures of about 200°C.

5 Due to the low cost of polyethyleneoxy and polypropyleneoxy polyols, it would be desirable to produce extrusion grade TPUs from such polyols which have good thermal processing characteristics. However, the formation of crystallites and gels is particularly a problem when the TPU resin is made by a reactive extrusion process and the diol contain secondary hydroxy groups. U.S. Patent Re. 31671 discloses a process for making thermoplastic  
10 polyurethane elastomers from polyoxyethylene polyoxypropylene polyols which have a certain oxyethylene group content. This process allows for the use of polyether polyols in processes for making thermoplastic polyurethanes which are processed at elevated temperatures, which have fewer problems with thermal processing than polyoxypropylene polyols which do not contain any ethylene oxide groups. However, the thermal stability of such thermoplastic  
15 polyurethanes may still be less than desirable for certain applications.

Further, continuous one-shot reactive extrusion processes tend to form high melting gel particles in the resin when the reactivity of the polypropyleneoxy/-polyethyleneoxy diol is lower than that of the chain extender. This circumstance arises when the diol is wholly or partially terminated by a secondary hydroxyl group, while the chain extender contains only  
20 primary hydroxyl functionality. The gel particles result from the formation of a broad distribution of hard-segment lengths, with the longer hard-segments having a higher melt temperature than typical extrusion process temperatures. Such gels are more likely to form under reactive extrusion process conditions than under low temperature batch process reaction conditions. It would be desirable to produce thermoplastic polyurethanes from  
25 polypropyleneoxy or polypropyleneoxy/polyethyleneoxy polyols, which have a crystalline melting point which does not substantially vary when the polymer is processed at elevated temperatures, and which can be extruded into films or other profiles which are substantially free of gel particles.

In one aspect, this invention is a thermoplastic polyurethane elastomer prepared  
30 by a reactive extrusion process from a reaction mixture comprising:

- (a) a polyisocyanate;
- (b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an equivalent weight of at least about 500; and
- (c) diethylene glycol;

35 wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1, and the ratio of isocyanate groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05.

It has been discovered that the composition of the invention provides an extrusion grade thermoplastic polyurethane resin. The resin is produced by a one-shot process which is preferably a continuous one-shot extrusion process, and is prepared from diols containing propyleneoxy groups. The resin has a stable crystalline melting point, and can be thermally processed and extruded into films or other profiles which are substantially free of gels.

Suitable diols for use as component (b) of the reaction mixture include polypropyleneoxy diols, polypropyleneoxy/polyethyleneoxy diols which contain up to about 50 percent by weight ethyleneoxy groups, and mixtures thereof. The equivalent weight of such diols is preferably at least about 500, more preferably at least about 750; and is preferably no greater than about 2000, more preferably no greater than about 1500.

Preferably, the diol is a polyoxypropylene/-polyoxyethylene block copolymer, which has been "capped" with ethylene oxide in order to have terminal primary hydroxyl groups. The ethylene oxide content of diol is preferably at least about 5 weight percent, more preferably at least about 10 weight percent; and is preferably no greater than about 40 weight percent, more preferably no greater than about 30 weight percent, based on the weight of the diol. In addition, the diol preferably contains an average of at least 21 propyleneoxy groups per molecule. Such diols are well-known materials, and are typically prepared by polymerizing propylene oxide, or ethylene oxide and propylene oxide in the presence of a hydroxy-functional initiator compound, such as a glycerine or water, and a catalyst, such as a tertiary amine, or a hydroxide or alkoxide of sodium and potassium. The quantities and types of alkylene oxide, and feed sequence (random or block) depend on the eventual equivalent weight and ethylene oxide content of the product to be prepared. In addition, if primary hydroxy-terminated diols are desired, the feed sequence will terminate with ethylene oxide.

Suitable polyisocyanates include 4,4'-methylenebis(phenyl isocyanate), 2,4-tolylene diisocyanate, isophorone diisocyanate, and 4,4'-diisocyanatodicyclohexylmethane, but is preferably 4,4'-methylenebis(phenyl isocyanate). Diethylene glycol is a well-known compound. Up to 25 percent, on a molar basis, of the diethylene glycol may be replaced with difunctional isocyanate-reactive materials with an equivalent weight of less than about 500 ("chain extenders"). Preferably, however, the diethylene glycol comprises at least about 90 mole percent of any chain extenders present in the reaction mixture, more preferably at least about 95 percent. Most preferably, however, no chain extender other than diethylene glycol is used. Examples of such additional chain extenders include 1,4-butanediol, 1,6-hexanediol, 1,4-bis(2-hydroxyethoxy) benzene (HQEE), and dipropylene glycol.

The term "isocyanate-reactive groups" as used herein refers to active hydrogen groups and carbodiimide groups. Active hydrogen-containing compounds include compounds containing at least one group which reacts positively in the well-known Zerewitinoff test. See

Kohler, Journal of the American Chemical Society, p. 3181, Vol. 49 (1927). Representative active hydrogen-containing groups include -OH, -COOH, -SH and -NHR where R can be hydrogen, alkyl, cycloalkyl and aryl aromatic.

The reaction mixture may be prepared by any suitable method for feeding  
5 thermoplastic polyurethane starting materials directly into an extruder, but is preferably prepared by directly feeding together at least two streams of starting materials into a self-wiping twin screw extruder in a one-shot process. A more preferred process is the continuous one-shot reactive extrusion process described in U.S. Patent 3,642,964. The reaction temperature may be any temperature which will allow the reaction between the starting  
10 materials to proceed, but the reactants are preferably combined at a temperature about the melting point of the diisocyanate, or in the range of from 25°C to 200°C, although the reaction mixture may reach higher temperatures in the extruder. While the polyurethane elastomers of the invention will harden at ambient conditions when cooled following the heating of the reaction mixture, the hardening process may be accelerated by the use of film extrusion  
15 techniques or lower cooling temperatures, particularly for polyurethanes in the 80 to 90 Shore A hardness range.

Preferably, the reactants are dried to less than about 150 ppm moisture, preferably less than about 50 ppm moisture, prior to mixing. This can be accomplished by conventional procedures, such as heating under reduced pressure until the water boils and is  
20 stripped off.

The ratio of isocyanate groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05. Preferably, the ratio is at least about 0.99; and is preferably no greater than about 1.03.

The polyurethane elastomers of this invention can be produced in a hardness  
25 range from 70 Shore A to 80 Shore D. The present polyurethane elastomers can remain at typical processing temperatures (for example 200°C) for at least about 30 minutes without significant increase in the crystalline melting point ( $T_m$ , measured by a differential scanning calorimeter operating at a constant rate of temperature rise, and defined as the highest temperature point where a local maximum exists in the measured heat absorption spectrum of  
30 the polymer) of the hard-segment of the resin, and can be extruded on conventional equipment into film, sheet, tubing, or other profiles. Preferably, the  $T_m$  will increase less than 10°C under such conditions, more preferably less than about 5°C. In addition, the polyurethane elastomers of the invention possess excellent tensile strength, high tear resistance, high elongation, and good low temperature flexibility.

35 A catalyst may be included in the reaction mixture to prepare the compositions of this invention. Any of the catalysts known in the art to catalyze the reaction of an isocyanate with a reactive hydrogen may be employed. Representative organometallic catalysts include stannous octoate, stannous oleate, dibutyltin dioctoate and dibutyltin dilaurate.

Representative tertiary amine catalysts include triethylamine, N,N,N',N'-tetramethylethylenediamine, N-methylmorpholine, N-ethylmorpholine and N,N'-diethylethanolamine. Catalysts are typically used in amounts ranging from 0.01 percent to 2 percent by weight in the polymer. A preferred catalyst is stannous octoate, used in the amount of 0.01 percent to 0.02 percent by weight.

Monofunctional chain terminators, such as n-octanol, stearyl alcohol, or butyl carbitol may be used in the synthesis of the TPU resins in accordance with this invention, for the purpose of limiting the molecular weight of the finished product. When a chain terminator is incorporated, the ratio of isocyanate groups to isocyanate-reactive groups preferably remains in the aforementioned range of 0.97 to 1.05.

The thermoplastic polyurethanes of this invention may contain other additives, added before or after polymerization, such as lubricants, waxes, stabilizers, fillers, dyes, pigments, plasticizers, flame retardants, or other compounds.

The thermoplastic polyurethanes of this invention may be melt processed by any of the conventional means, for example, compression molding, transfer molding, injection molding, cast film extrusion and blown film extrusion. Formulations having a Shore A durometer of less than about 90 when based on a polyol with a molecular weight less than about 2000 tend to require long molding cycles, to allow the TPU resin time to cool completely before demolding. These same formulations, however, may be extruded at conventional production rates into profiles having a thickness less than about 2 mm because these thin extrudates can be quickly cooled. Melting and plastication of the TPU resins of this invention may be satisfactorily accomplished in conventional single screw extruders, twin screw extruders, planetary gear extruders, and other equipment designed for polymer processing. Generally, homogeneous melts free from gel particles can be obtained under a wider range of process conditions than is the case for conventional polyether TPU resins, even those from poly(tetramethylene ether) glycol.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages of chain extenders and other components are given by molar equivalents, based on one molar equivalent of polyol.

The polyurethanes in the Examples 1-4 are prepared by charging the polyol, chain extender(s), and additives such as wax and anti-oxidant to a tank where they are heated to 115°C and stripped under vacuum to remove moisture. After about 4 hours of stripping, the polyol/chain extender mixture is metered into the feed port of an intermeshing, self-wiping, counter-rotating twin screw extruder along with a stoichiometric amount of 4,4'-diphenylmethane diisocyanate (Isonate™ 125M, available from The Dow Chemical Company) and 0.02 weight percent of stannous octoate catalyst. The twin screw extruder is operated at a screw speed of 450 rpm, with a typical barrel temperature profile of:

5	Feed Zone	1	220°C
	Zone	2	215°C
	Zone	3	180°C
	Zone	4	180°C
	Zone	5	180°C
	Zone	6	180°C
	Zone	7	180°C
	Zone	8	190°C

10

Upon exiting the extruder, the polymer is cast onto a moving belt to effect cooling. The resulting web, having dimensions about 8 inches wide by 1/8 inch thick, is granulated and dried in a desiccant bed dryer prior to molding and extrusion.

15

Physical properties of the polymers are measured from injection molded plaques approximately 1/16 inch thick. The molded plaques are allowed to cure 3 days at ambient conditions prior to testing.

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Extrusion characteristics of the polymers are evaluated by producing cast films 10 mils thick from a 1.5 inch 24:1 L/D single screw extruder with a 12 inch wide flat sheet die (Chippewa Valley Die Inc., Masterflex R/Ld-75) and 3-roll stack. Extrusion conditions are noted below.

25

Stability of the crystalline melt temperature is determined by differential scanning calorimetry (DSC). Polymer samples are heated to 200°C at a rate of 20°C/minute in a DuPont Model 2100 DSC, then held isothermally at 200°C for 30 minutes. The sample is then slowly cooled to ambient temperature, and re-heated at 20°C/minute until completely molten. If the highest temperature melting endotherm on the second heat is more than 10°C greater than the highest temperature melt from the first heat, then the crystalline melting temperature of the polymer may increase during extrusion processing and cause unmelted polymer chunks to become entrained in the extrudate. Such a TPU resin is listed as "unstable."

30

The following diols (all available from The Dow Chemical Company) are used in the examples:

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DiolsDESCRIPTION

- A a polypropyleneoxy glycol capped with 10 percent by weight ethylene oxide, with an average molecular weight of about 2000
- B a polypropyleneoxy glycol capped with 20 percent by weight ethylene oxide, with an average molecular weight of about 1500
- C a polypropyleneoxy glycol, with an average molecular weight of about 1000
- D a polypropyleneoxy glycol capped with 40 percent by weight ethylene oxide, with an average molecular weight of about 4000

Example 1

A TPU resin composed of 1.0 equivalent of polyol A, 4.0 equivalents of diethylene glycol, and 5.0 equivalents of Isonate™ 125M was produced via the continuous one-shot reactive extrusion process. Physical properties of this TPU resin taken from injection molded plaques are listed below.

<u>Property</u>	<u>Units</u>	<u>ASTM Method</u>	<u>Value</u>
Durometer	Shore A	D 2240	83
Tensile Strength	MPa	D 412	17.2
Ultimate Elongation	%	D 412	650

The inflection point of the glass transition temperature measured by DSC was -41°C. The crystalline melting point is 155°C on the first heat, and 162°C on the second heat after cooling down from 30 minutes at 200°C. The crystalline melting point of the TPU resin from Example 1 is therefore found to be stable.

Example 2

A TPU resin composed of 1.0 equivalent of polyol B, 4.3 equivalents of diethylene glycol, and 5.35 equivalents of Isonate™ 125M was produced via the continuous one-shot reactive extrusion process. Physical properties of this TPU resin taken from injection molded plaques are listed below.

<u>Property</u>	<u>Units</u>	<u>ASTM Method</u>	<u>Value</u>
Durometer	Shore A	D 2240	94
Tensile Strength	MPa	D 412	35.5
Ultimate Elongation	%	D 412	425

The inflection point of the glass transition temperature measured by DSC is -12°C. The crystalline melting point was 132°C on the first heat, and 135°C on the second heat after

cooling down from 30 minutes at 200°C. The crystalline melting point of the TPU resin from Example 2 is therefore found to be stable.

Example 3 (Comparative Example)

A TPU resin composed of 1.0 equivalents of polyol C, 0.842 equivalents of 1,4-bis(2-hydroxyethoxy) benzene, 0.066 equivalents of dipropylene glycol, and 1.927 equivalents of Isonate™ 125M was produced via the continuous one-shot reactive extrusion process. Physical properties of the TPU resin produced are listed below:

	<u>Property</u>	<u>Units</u>	<u>ASTM Method</u>	<u>Value</u>
10	Durometer	Shore A	D 2240	83
	Tensile Strength	MPa	D 412	11.7
	Ultimate Elongation	%	D 412	475

The inflection point of the glass transition temperature measured by DSC is -15°C.

15 The crystalline melting point is 180°C on the first heat, and 189°C on the second heat after cooling down from 30 minutes at 200°C. The crystalline melting point of the TPU resin from Example 3 is therefore found to be stable.

Example 4 (Comparative Example)

A TPU resin composed of 1.0 equivalents of polyol B, 3.5 equivalents of 1,4-butanediol, and 4.545 equivalents of Isonate™ 125M was produced via the continuous one-shot reactive extrusion process. Physical properties of the TPU resin produced are listed below.

	<u>Property</u>	<u>Units</u>	<u>ASTM Method</u>	<u>Value</u>
25	Durometer	Shore A	D 2240	83
	Tensile Strength	MPa	D 412	22.1
	Ultimate Elongation	%	D 412	675

The inflection point of the glass transition temperature measured by DSC was -22°C. The crystalline melting point was 180°C on the first heat. On the second heat after cooling down from 30 minutes at 200°C, the polymer exhibited two distinct melting points at 188°C and 225°C. The crystalline melting point of the TPU resin from Example 4 was therefore found to be unstable.

35

	<u>TPU from Example</u>	<u>Melt Temperature</u>	<u>Film Quality</u>
5	1	180 to 205°C	Smooth, no gels
	2	190 to 215°C	Smooth, no gels
	3	180 to 210°C	Rough, with numerous gels
	4	180 to 200°C	Moderate gels

10 Due to its crystalline instability, the extrusion run using the TPU from Example 4 was interrupted when the die gap became plugged with unmelted, crystalline material.

The above data shows that diethylene glycol may be used as a chain extender to prepare thermoplastic polyurethane resins by a reactive extrusion process which have a stable crystalline melting point, and which are substantially free of gel particles. Example 1 may be  
 15 compared to Comparative Examples 3 and 4, which are all resins with a hardness of 83 Shore A. Example 1 produced a resin with a stable crystalline melting point temperature and which was extruded to produce a smooth film free of gels. Comparative Example 3, which employed, 1,4-bis(2-hydroxyethoxy) benzene, 0.066 equivalents of dipropylene glycol as co-chain  
 20 extenders, produced a resin which had a stable crystalline melting point temperature, but which extruded into a rough film, with numerous gel particles. Comparison Example 4, which employed 1,4-butanediol as the chain extender, produced a resin which did not have a stable crystalline melting point temperature, and was extruded into a film, with a moderate amount of gel particles. The gel particles described herein are visible to the naked eye in cast films 10  
 25 mils thick, and appear as distinct small, round, clear particles in the film.

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CLAIMS:

1. A thermoplastic polyurethane elastomer prepared by a reactive extrusion process from a reaction mixture comprising:
  - (a) a polyisocyanate;
  - (b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an  
5 equivalent weight of at least about 500; and
  - (c) diethylene glycol;wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1, and the ratio of isocyanate groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05.
- 10 2. The elastomer of Claim 1 wherein component (b) of the reaction mixture is a polypropyleneoxy diol.
3. The elastomer of Claim 1 wherein component (b) of the reaction mixture is a polypropyleneoxy/-polyethyleneoxy diol with an ethylene oxide content of between 10 to 30 weight percent, based on the weight of the diol.
- 15 4. The elastomer of Claim 1 wherein the polyisocyanate is 4,4'-  
-methylenebis(phenyl isocyanate).
5. A thermoplastic polyurethane elastomer prepared by a reactive extrusion process from a reaction mixture comprising:
  - (a) a polyisocyanate;
  - 20 (b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an equivalent weight of at least 500; and
  - (c) at least one chain extender comprising at least 75 mole percent diethylene glycol;wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1; the ratio of isocyanate  
25 groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05; and (c) is the sole chain extender component in the reaction mixture.
6. The elastomer of Claim 7 wherein component (c) comprises at least 95 mole percent diethylene glycol.
7. The elastomer of Claim 7 wherein the chain extender consists of diethylene  
30 glycol.
8. The elastomer of Claim 8 wherein the polyisocyanate is 4,4'-  
-methylenebis(phenyl isocyanate).
9. A process for preparing a thermoplastic polyurethane resin which comprises mixing the following in a screw extruder under reaction conditions sufficient to form the  
35 corresponding polyurethane resin:
  - (a) a polyisocyanate;
  - (b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an equivalent weight of at least 500; and

(c) at least one chain extender comprising at least 75 mole percent diethylene glycol;

wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1; the ratio of isocyanate groups to isocyanate-reactive groups in the mixture is in the range of from 0.97 to 1.05; and (c) is the sole chain extender component in the mixture.

10. A process for preparing a thermoplastic polyurethane resin which comprises mixing the following in a screw extruder under reaction conditions sufficient to form the corresponding polyurethane resin:

(a) a polyisocyanate;

(b) a polypropyleneoxy diol or a polypropyleneoxy/polyethyleneoxy diol with an equivalent weight of at least 500; and

(c) diethylene glycol;

wherein the molar ratio of (c) to (b) is in the range of from 2:1 to 20:1, and the ratio of isocyanate groups to isocyanate-reactive groups in the reaction mixture is in the range of from 0.97 to 1.05.

# INTERNATIONAL SEARCH REPORT

Int. Appl. No.

PCT/US 93/12483

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C08G18/66 C08G18/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 010 146 (RUSSELL ET AL) 1 March 1977 see column 1, line 51 - column 2, line 58; claims 1-4; examples 4,5	1-10
A	US,A,4 126 742 (CARLETON ET AL) 21 November 1978 see column 2, line 56 - column 3, line 59; claims 1,3,4; examples B,I	1-10
A	EP,A,0 320 946 (DOW) 21 June 1989 see claims 1-3; example 2	1
A	US,A,RE31671 (BONK ET AL) 11 September 1984 cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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